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review

OF RECENT
DEVELOPMENTS

Refractory Metals (Cb, Ta, Mo, W)

J. Van Orsdel, D. J. Maykuth, and V. D. Barth • April 16, 1969

COLUMBIUM

The procedures developed for redrawing columbium alloy D-43 tubing of 60-foot lengths, 0.125 inch ID, and 0.006-inch wall thickness, are described in a Whittaker report.⁽¹⁾ The D-43 redraw tubing stock was in 5 to 12-foot lengths of 0.310-inch OD, and 0.030-inch wall thickness.

Most of the redraw work employed conventional tube-drawing dies; however, an investigation was also made of planetary ball swaging for tube reducing. In general, the ball-swaging technique was found to give less satisfactory results than conventional drawing. Flaking of the tube surface was a problem during ball swaging at speeds of 400 rpm; at lower speeds, there was a tendency for the balls to form spiral grooves in the tube.

In conventional die-mandrel drawing tests, lubrication was found to be of particular importance in preventing galling and sticking of the columbium alloy to the tooling. Hangsterfer's "112QD" and "Aldraw J-2", which are commercial lubricants, were found to be satisfactory to overcome this problem.

Although the first drawing trials demonstrated the possibility of drawing the annealed stock tubes to final size (an area reduction of 91 percent) without interpass anneals, the material yield was low. Optimum processing was established with one intermediate anneal in the draw schedule plus one solution-and-age treatment before the final sinking passes. A total of 12 tubes were drawn. Finished lengths varied from 33 to 68 feet, with nine tubes greater than 60 feet in length. Six of the 12 tubes were free of defects. Mechanical properties of D-43 tubing before and after various heat treatments are summarized in Table 1.

The initial concern of a program at Solar on the structural effects of interstitial sinks was with the changes in structure, strength, and interstitial concentration in a refractory alloy induced by an interstitial sink. The scope was later broadened to include the effect of interstitial and substitutional solutes on the creep of columbium- and tantalum-base alloys. The current approach is to study the influence of solutes on creep strength through their effect on the activation energy.⁽²⁾ The factors affecting the activation energy for creep of several columbium alloys have been investigated, and the activation energies have been determined over the 1800 to 2800 F range as shown in Figure 1.

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Sticking probabilities for oxygen on columbium and dilute columbium-zirconium alloys were derived at the Lewis Research Center from ratios of oxygen absorption rates to their corresponding oxygen fluxes.⁽³⁾ Oxygen test pressures were varied from 10^{-7} to 10^{-5} torr over temperatures ranging between 1158 to 1373 K (1625 to 2012 F). The sticking probabilities derived from a regression analysis of

TABLE 1. AVERAGE MECHANICAL PROPERTIES OF D-43 TUBING BEFORE AND AFTER HEAT TREATMENT⁽¹⁾

Condition	Ultimate Tensile Strength, ksi	0.2% Offset Yield Strength, ksi	Elongation, (1-in. gage length), percent
As-received and annealed (0.310-in. OD x 0.030-in. wall)	70.3	40.8	28.4
Drawn 82% to 0.241-in. OD x 0.007-in. wall	125.8	109.7	1.7
Ditto + 1800 F, 1 hr	152.2	126	5.0
Ditto + 2000 F, 1 hr	123.7	83.2	11.0
Ditto + 2200 F, 1 hr	83.4	53.8	21.3
Ditto + 2400 F, 1 hr	83.3	53.0	13.0
Ditto + 2600 F, 1 hr	78.7	48.2	22.3

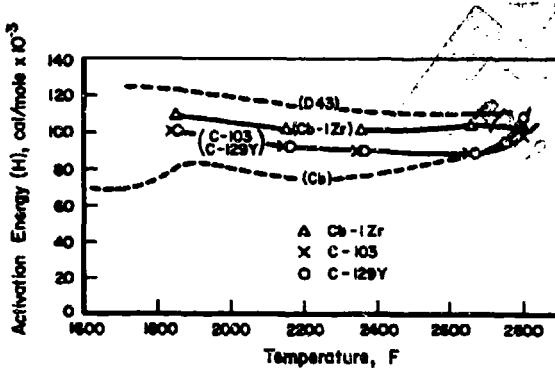


FIGURE 1. THE ACTIVATION ENERGY FOR CREEP OF COLUMBIUM AND SOME COLUMBIUM ALLOYS OVER A RANGE OF TEMPERATURES⁽²⁾

the data were 0.047 to 0.093 for columbium and Cb-1Zr in the hot-wall case, and 0.077 to 0.15 for columbium and Cb-1Zr in the cold-wall case.

TRW reports continued progress in an Air Force-sponsored program to develop columbium-alloy combinations of high-strength core alloys encased in an oxidation-resistant alloy for composite blading in short-term gas turbines operating near 2200 F.⁽⁴⁾ The potential core alloys being evaluated are Cb-132M, VAM-79, and SU-31 whose nominal compositions are as follows:

Alloy	Cb	Ta	W	Mo	Zr	Hf	C
Cb-132M	Bal	20	15	5	1.5	--	0.12 to 0.20
VAM-79	Bal	--	22	--	--	2	0.067
SU-31	Bal	--	17	--	--	3.5	0.12

Material has been forged to simulate a blade-forming operation. Various thermal-mechanical processes have been utilized. Recrystallization, grain coarsening, and carbide solutioning and precipitation behavior were found to vary significantly among the three alloys. In 1200 F tensile tests, the Cb-132M alloy exhibited superior 0.2% yield and tensile strengths, with comparable ductility with the other alloys. Diffusion-bonding studies showed that satisfactory bonds can be obtained at 2200 F between Cb-10Ta-10W-1Zr sheet and annealed Cb-132M plates. Samples bonded at 2200 F showed a smaller degree of carbon migration from the Cb-132M than those bonded at 2400 F. Bonding was facilitated by the use of a vanadium-foil intermediate layer.

COLUMBIUM-TANTALUM

The effects of hydrogen environments on columbium and tantalum alloys are discussed in a final report from Rocketdyne.⁽⁵⁾ The materials studied were columbium, B-66 (Cb-5Mo-5V-1Zr) alloy, tantalum, and Ta-10W alloy.

Tantalum and Ta-10W were tensile tested in argon and H₂O/H₂ mixtures at 1 atmosphere in the range 400 to 1500 F. The elongation of both materials was drastically reduced in H₂O/H₂ at higher temperatures. Columbium, B-66 alloy, tantalum, and Ta-10W alloy were tensile tested in hydrogen at 800 and 1500 psi to determine the ductile-brittle transition temperature. The transition-temperature range was 1100 to 1200 F for columbium, 1200 to 1300 F for tantalum, and 1700 to 1800 F for B-66 alloy, with no significant effect of hydrogen pressure. The transition-temperature range for Ta-10W alloy was 1500 to 1600 F in hydrogen at 800 psi and 1700 to 1800 F in hydrogen at 1500 psi. The solubility and absorption-desorption rates of hydrogen in columbium, B-66 alloy, tantalum, and Ta-10W alloy also were measured at 800 and 1500 psi between 600 and 1800 F. The solubility increased approximately two-fold from 800 to 1500 psi. There was no direct correlation between solubility and the ductile-brittle transition temperature. Diffusion rates were calculated from desorption data. Similar diffusion coefficients in the range of 10⁻⁵ cm²/sec were obtained for all the materials.

This study indicated that, of the materials tested, the B-66 and Ta-10W alloys showed the smallest tendency to crack in hydrogen. However, these two alloys would require protective coatings for use in H₂O/H₂ environments at 1 atmosphere, above about 1000 F. The ductile-brittle transition temperatures were higher than expected for the B-66 and

2
Ta-10W alloys (greater than 1500 F), indicating that a protective coating also would be required to use these materials in hydrogen environments at 800 and 1500 psi.

COLUMBIUM-MOLYBDENUM

A study of twinning and its effect on the low-temperature mechanical properties of polycrystalline columbium, molybdenum, and columbium-molybdenum alloys is being conducted at Westinghouse.⁽⁶⁾ Compression and tension testing has been performed over a range of temperatures encompassing the ductile-brittle transition temperature on irradiated and non-irradiated molybdenum and three columbium-molybdenum alloys. Stress-relaxation tests in conjunction with these were interpreted to show that gross slip and twinning are not involved in the initiation of fracture under conditions where the alloys fracture in a brittle manner. Also, irradiation damage and alloying evidently acted in a similar manner in inhibiting slip and twinning. Using a strain-gage bridge for measurement, no slip was found to take place within 2 x 10⁻⁴ seconds of fracture, and gross twinning took place entirely within 2 x 10⁻⁴ seconds in both polycrystalline and single-crystal specimens. The propagation energy was concluded to be a predominant factor in twinning.

MOLYBDENUM-HAFNIUM

The results of a preliminary study on the properties and heat treatment of molybdenum-hafnium alloys were reported by Lewis Research Center.⁽⁷⁾ Nine alloys, containing up to 1.83 atomic percent hafnium and 1.07 atomic percent carbon, were prepared by consumable-electrode arc melting, extrusion, and swaging to bar stock of 1/4-inch diameter. The properties evaluated included recrystallization behavior, heat-treatment response, and tensile, creep, and stress-rupture strengths at temperatures to 3000 F.

Useful combinations of room-temperature ductility and hot strength were shown in most of these alloys as indicated in Table 2, which compares tensile properties for a few of these alloys with those of the commercial TZM and TZC alloys. A further comparison of the stress-rupture strengths of these alloys in the as-wrought or stress-relieved condition at 2400 F (vacuum of less than 5 x 10⁻⁵ torr) is given below:

Alloy Composition, atomic percent	Stress to Cause Rupture in 50 Hours, ksi
Mo-0.18Hf-0.42C	40.5
Mo-0.39Hf-0.65C	35.5
Mo-CbTZC	33
Mo-TZC	24 to 30.5
Mo-TZM	14

Collectively, these results suggest that the molybdenum-hafnium-carbon alloys have a strength advantage over the existing TZC and TZM alloys in stress-rupture tests at 2400 F and in short-time tensile tests at 3000 F. This strength advantage was tentatively attributed to the higher thermodynamic stability of HfC as compared with the carbides found in the other alloys.

Heat-treatment experiments showed that the 2400 F tensile strengths of the molybdenum-hafnium-

3
TABLE 2. TENSILE PROPERTIES OF SELECTED Mo-Hf-C AND TZM AND TZC ALLOYS⁽⁷⁾

Alloy Content, atomic percent	Test Temperature, F	Tensile Properties							
		As Wrought or Stress Relieved				As Recrystallized			
		UTS, ksi	YS, ksi	Elong., percent	RA, percent	UTS, ksi	YS, ksi	Elong., percent	RA, percent
Mo-0.18Hf-0.42C	RT	--	--	4	3	80.1	54.4	38	49
	2400	71.4	68.9	12	59	33.6	17.9	48	78
	3000	25.6	24.9	22	98	13.7	8.8	65	98
Mo-0.39Hf-0.65C	RT	151	139	12	31	86.9	60.6	35	44
	2400	70.7	67.7	18	57	35.3	22.6	37	85
	3000	21.2	19.5	20	88	15.1	10.1	59	98
Mo-0.96Hf-0.82C	RT	195	145	8	8	90.4	56.2	27	37
	2400	66.8	64.2	14	67	46.4	28.1	24	79
	3000	29.1	27.3	25	76	15.4	14.5	39	93
Mo-TZM ^(a)	RT	108.7	105.4	28	75	--	--	--	--
	2400	47.8	46.3	18	>98	--	--	--	--
	3000	10.3	7.6	75	>98	--	--	--	--
Mo-TZC ^(b)	RT	112.1	98.8	30	59	--	--	--	--
	2400	47.1	46.5	18	86	--	--	--	--
	3000	22.2	21.8	35	>98	--	--	--	--

(a) Commercial heat; composition in weight percent was Mo-0.5Ti-0.096Zr-0.016C.

(b) Commercial heat; composition in weight percent was Mo-1.2Ti-0.17Zr-0.11C.

carbon alloys could be further increased by appropriate solution treatments and/or prestraining at 3000 F.

TANTALUM

A final report has issued by Aerojet on the demonstration of a submerged cooled nozzle, using lithium as an evaporative coolant.⁽⁸⁾ Tantalum alloy T-222 was evaluated for the 5-inch-diameter throat of the nozzle. Thermal and mechanical properties of this alloy were characterized to provide accurate design data. Table 3 shows the strength superiority of the T-222 alloy over Ta-10W in the 2500 to 4000 F range. One-minute creep data for a single heat of T-222 alloy are given as follows:

Temperature, F	Stress, psi	One-Minute Creep, percent
3000	15,760	1.2
3000	13,090	0.8
3000	15,280	1.2
3500	12,630	2.3
3500	10,580	0.7
4000	3,470	0.2
4000	5,500	2.3
4000	6,820	3.1

These results were considered adequate justification for using T-222 alloy for the nozzle throat material in the program.

TUNGSTEN

The structural behavior of tungsten and tungsten-base alloys in a cyclic heating environment resembling the thermal environment of a restartable rocket motor has been investigated in a study conducted at TRW Systems.⁽⁹⁾ Hollow cylindrical specimens of arc-cast tungsten, extruded tungsten, extruded W-2ThO₂, and extruded W-26Re were rapidly heated from the inner surfaces and the thermal, deformation, and microstructural histories were examined. Wrought tungsten was found to be the most dimensionally stable. Arc-cast tungsten underwent

TABLE 3. TENSILE PROPERTIES OF RECRYSTALLIZED T-222 AND TA-10W SHEET ALLOYS AS A FUNCTION OF TEMPERATURE⁽⁸⁾

(Average values of two specimens 0.130-inch thick at each temperature.)^(a)

Temp., F	T-222 Alloy		Ta-10W Alloy	
	Ultimate Tensile Strength, ksi	0.2% Offset Yield Strength, ksi	Ultimate Tensile Strength, ksi	0.2% Offset Yield Strength, ksi
75 ^(b)	117.2	106.5	--	--
2500	45.6	39.0	36.5	30.0
3000	27.8	25.5	21.9	19.7
3500	16.5	16.0	12.4	11.1
4000	8.2	3.9	7.5	7.3
3000 (in air)	24.3	19.1	19.5	17.9

(a) Strain rate: 0.1 inch/inch/minute; atmosphere: helium; heating method: direct resistance.

(b) 0.005 inch/inch/minute strain rate.

extremely large deformations when subjected to short-duration pulses (0.8 second). Thoriated tungsten was the most stable from a microstructural point of view, although a thermal pretreatment was necessary for both this alloy and the arc-cast material to survive the initial heating pulse without cracking. The W-26Re alloy approximated arc-cast and thoriated tungsten in dimensional behavior, but did not require the same thermal pretreatment. The agreement between experimentally determined deformations and those predicted analytically was quantitatively very good, and demonstrated an analytical approach capable of synthesizing materials for rocket-hardware applications.

In a Lawrence Radiation Laboratory study, tungsten, W-25 wt% Re, and W-30 wt% Re alloys were

plastically deformed in the 1400 to 1900 C (2550 to 3450 F) temperature range at creep stresses up to 10,000 psi in a vacuum of less than 10^{-8} torr.(10)

For tungsten, the activation energy for creep was calculated to be about 100 kcal/mole, i.e., considerably less than an earlier value of 140 kcal/mole found for volume self diffusion. The rate-controlling deformation mechanism during creep was ascribed to dislocation climb. For W-25 wt% Re alloy, two distinct rate-controlling mechanisms, dependent on grain size, were operative, with activation-energy values of 100 and 62 kcal/mole corresponding to dislocation glide and grain-boundary sliding, respectively. Solid-solution alloying of tungsten with rhenium was ineffective in promoting creep resistance. The activation energy for W-30 wt% Re also amounted to 100 kcal/mole, and was associated with the dislocation glide model. Creep strength in this last alloy was not enhanced by sigma-phase precipitates in grain boundaries.

The yield strength of a dispersion-hardened W-3.8 wt% ThO₂ alloy in both the recovered and recrystallized conditions was examined by King, and was compared with those of pure tungsten over the 325 to 2400 C (617 to 4350 F) temperature range.(11) Results for the recrystallized alloy indicated that Orowan's mechanism for fine-particle strengthening is obeyed during yield. In the recovered alloy, yield strength was further enhanced by the retained substructure which is stable up to temperatures in excess of 2700 C (4890 F). The yield stress of the alloy in the recovered state was greater by a factor of about 5 than that of recrystallized pure tungsten. After recrystallizing the alloy at 2850 C (5160 F), the yield strength was greater by a factor of 2 than that for pure tungsten annealed at the same temperature. Contributions to the yield stress of a dispersion-hardened alloy are believed to come from the yield stress of the single crystal matrix, the Orowan-related yield stress, and the substructure-related yield stress.

According to Conway, the Manson-Haferd parameter yields more effective representation of stress-rupture data in the 1200 to 3000 C (2190 to 5430 F) temperature range for tungsten and some other refractory materials than do the Larson-Miller or Dorn parameters.(12) Commonly, the value of the constant, C, in the Larson-Miller expression, $P = T(C + \log t)$, is taken as 20, where t represents time at a particular stress level for a given strain or fracture. In fact, C was found to range, for example, from 12.3 to 20.3 for the creep of arc-cast tungsten, depending on the amount of strain involved.

Raffo has reported that the characteristic reduction in the ductile-brittle transition temperature of tungsten by additions of rhenium appears to arise from the increased plastic strain possible at crack tips as a result of increased dislocation mobilities and multiplication rates.(13) The reduction of temperature and strain-rate dependency of the yield stress through rhenium additions infers a reduction of the Pierls stress which makes such mobility increase possible.

The scavenging of oxygen from dislocation and grain-boundary sites by rhenium in solid solution in tungsten appears probable, and is believed by Novick and Machlin to be the basis of the increment in ductility known to be associated with the

addition of rhenium to tungsten.(14) The assumption that rhenium acts to increase the lattice solid solubility by the formation of ReO complexes was found to be in quantitative agreement with data derived from field-ion-microscope observations.

Elongations as high as 260 percent have been observed in W-23 at.% Re alloy when tensile tested at 3630 F after a 1-hour anneal at 3090 F.(15) All alloys tested under these conditions with rhenium contents between 20 and 28 atomic percent exhibited elongations of at least 200 percent. The equiaxiality of grains in the deformed sections of tensile specimens showing high elongations suggests that grain-boundary sliding contributes significantly to deformation.

The time-temperature dependence for the first variation of deformation structure in hard-rolled tungsten, as well as for the onset and termination of primary recrystallization, has been established by metallographic means in European work.(16) Figure 2 summarizes the data obtained. (Curve A represents the first variation in structure, with a related activation energy of 68 kcal/g-atom.) The activation energy associated with the beginning of recrystallization was about 150 kcal/g-atom, i.e., approximately the same as for volume self diffusion.

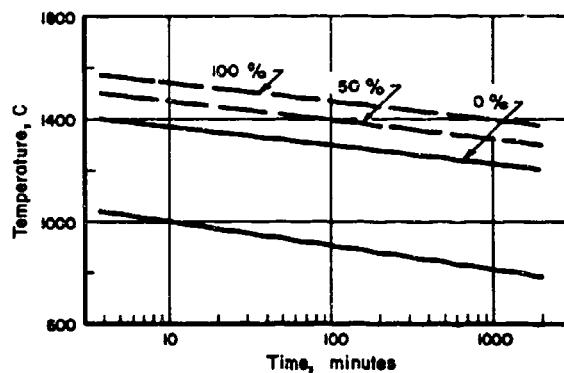


FIGURE 2. TIME-TEMPERATURE CURVE FOR THE RECRYSTALLIZATION OF TUNGSTEN(16)
(Curve A represents the first variation in structure.)

The solubility of nitrogen in tungsten has been redetermined.(17) In the 2400 to 3050 C (4350 to 5520 F) temperature range, the following relation is applicable:

$$C_N = \sqrt{p_{N_2}} \cdot 700 \exp \left(-\frac{46,700}{RT} \right)$$

where C_N is dissolved nitrogen in ppm, p is nitrogen pressure in torr, and T is absolute temperature in degrees Kelvin.

The diffusion of nickel in tungsten is markedly structure sensitive.(18) In a study of both fibrous and 2300 C (4170 F) recrystallized, doped specimens, no significant amount of nickel could be introduced into the doped specimens at 1200 C (2190 F). The bulk diffusivity into recrystallized tungsten was estimated to be less than 10^{-11} cm²/sec at this temperature. Diffusion into fibrous

material led to recrystallization. Continued accumulation of nickel was blocked, however, by the arrival of the recrystallization front.

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- material led to recrystallization. Continued accumulation of nickel was blocked, however, by the arrival of the recrystallization front.

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